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Heterogeneous acid conversion of a tricaprylin-palmitic acid mixture over Al-SBA-15 catalysts: Reaction study for biodiesel synthesis

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ABSTRACT

In this work mesoporous Al-SBA-15 was synthesized by the sol-gel method and used as a solid acid catalyst for the conversion of a model mixture of tricaprylin with 20 wt% of palmitic acid at T = 175–215 °C. The incorporation of aluminum to the SBA-15 through the sol-gel method, gives rise to mesoporous materials with the typical hexagonal arrangement of SBA-15 (XRD). In addition, these materials possess Lewis and Brönsted acid sites (pyridine adsorption), large surface area and wide pore diameter (N_2 physisorption) being capable of catalyzing simultaneously transesterification of triglycerides (tricaprylin) and esterification of palmitic acid (up to 20 wt%) resulting in FAME yields of 40–87%. A detailed analysis of the reaction products indicates that the conversion of triglyceride to diglyceride is the limiting step during the acid transesterification over Al-SBA-15 catalysts, which results from the difficulty to protonate triglycerides followed by methanol addition. A simplified lumped first order reaction model reproduces well the experimental data for the acid transesterification of tricaprylin in the presence of a high content of free fatty acids (palmitic acid). The calculated activation energy was 64.7 kJ mol^{-1} which is in the range of 45–120 kJ mol^{-1} previously reported for acid catalysts.

1. Introduction

Traditional homogeneous basic catalysts, even with large reaction rates, are unable to perform simultaneously esterification and transesterification reactions because of the presence of free fatty acids (FFAs) and water [1]. The presence of water favors the formation of FFAs by hydrolysis of triglycerides (TGs) [2], besides FFAs with homogeneous basic catalysts also gives rise to soap formation, making difficult the separation of products and diminishing the activity of the catalysts [1].

In this context, heterogeneous acid catalysts represent an interesting option, because both esterification and transesterification reactions could occur through an acid route [3]. Therefore, several types of heterogeneous acid catalysts have been investigated for the transesterification of different vegetal and animal lipids. These catalysts include zeolites, which are materials whose surface acidity can be modulated with the addition of different atoms to the aluminosilicate structure [4]; despite of that, zeolites have exhibited low catalytic activity, which has been mainly associated with the restricted transport of TGs into their cavities [5]. Supported heteropoly acids are also materials with strong Brönsted acidity, but their solubility in methanol limits their use for several reaction cycles [6]. Additionally, some resins as Amberlyst 15 have provided good yields for esterification under mild conditions because of their open structure; however, they exhibited low activity for transesterification due to their poor thermal stability at high temperatures [6]. Some other catalysts like superacids, which are materials that use zirconium, titanium and tin oxides as supports, and sulfate or tungsten compounds as active phases [7–9], have been also used for the simultaneous esterification and transesterification, however the leaching of the sulfate compounds from the catalyst was commonly observed [9]. Analyzing these previous works, it can be concluded that large pore diameter, strong acidity, thermal stability and surface hydrophobicity are desirable properties for acid catalysts in order to improve the diffusion of reactants and products and to repel the water, which is formed during the esterification reaction [10].

Therefore, an interesting alternative is the use of amorphous silica with ordered mesoporous structure, such as SBA-15. These materials exhibit a large pore size, high thermal stability

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and hydrophobic nature. In addition, their acid properties can be modified with the incorporation of metals like aluminum, titanium and zirconium [3,11,12]. Some previous studies regarding mesoporous materials have reported simultaneous esterification and transesterification of vegetable oils employing high reaction temperatures and elevated methanol/oil molar ratio without leaching of the active phase [3,11,12]. Nevertheless, there are only few reaction studies related to the heterogeneous acid transesterification and less in the presence of high concentrations of FFAs. López et al. [13] studied the esterification and transesterification of a mixture consisting of tricaprylin-oleic acid (7 wt.%) over modified-zirconia catalysts at 120 °C. According to this study, esterification is easily performed and tricaprylin conversion proceeded not only by transesterification but also by hydrolysis due to the presence of water produced during the esterification of oleic acid. However, there is not a clear understanding about the necessary reaction conditions, determining reaction step, and the role of Lewis and Brönsted acid sites in the transesterification of raw materials with high content of FFAs.

Thus, in this work, the behavior of Al-SBA-15 catalysts in the acid heterogeneous conversion of a tricaprylin-palmitic acid (20 wt%) mixture is analyzed. The model mixture was used in order to simulate waste cooking oils as raw material for biodiesel production. The reaction study was conducted at 175–215 °C, allowing to estimate the reaction rate constant for each temperature and the activation energy of the reaction. The physicochemical properties of the catalysts were studied by XRD, pyridine adsorption analyzed by FT-IR and N_2 physisorption. Additionally, the importance of mass transport limitations was theoretically assessed, and a simplified scheme of the main reaction pathways was proposed.

2. Experimental

2.1. Materials

High purity commercial chemicals were used for the synthesis of catalyst and for reaction tests, namely, Tetraethyl orthosilicate (TEOS, 98%), non-ionic triblock copolymer PEO-PPO-PEO ((poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)) (pluronic P123, W:5800 g/mol), aluminum isopropoxide (AIP, 98%) and glyceryl trioctanoate (Tricaprylin, TCp, ≥99%) from Sigma-Aldrich. Additionally, hydrochloric acid (HCl, 37%), hexanes (hexane, 95%), palmitic acid (HPa, ≥99%), methanol (MeOH, 99.8%) and sodium sulfate anhydrous powder (Na_2SO4, 99%) from J.T. Baker.

2.2. SBA-15 and Al-SBA-15 synthesis and characterization

SBA-15 was synthesized using Pluronic P123 as structure-directing agent and TEOS as silica source. In a typical process, 4 g of P123 were dissolved in 150 mL of aqueous HCl setting pH at 1.5 (0.0316 M). Subsequently, 5 mL of TEOS was added dropwise to the solution. After stirring at 40 °C for 24 h, the mixture was aged at 90 °C for 24 h. After that, the white precipitate was filtered and dried at 110 °C overnight, and then it was calcined in air at 550 °C for 6 h using a heating rate of 1 °C min^{-1}.

Al-SBA-15(x) catalysts, where x represents the SiO_2/Al_2O_3 molar ratio of 20 and 40, were synthesized through the sol-gel method under acid conditions, as described by Liang et al. [14]. In a typical procedure, 5 mL of TEOS and the corresponding amount of AIP were added to 10 mL of aqueous HCl (0.0316 M) at pH of 1.5 to obtain a SiO_2/Al_2O_3 molar ratio of 20 and 40. The solution was stirred for 3 h and then added to a second solution containing 4 g of P123 in 140 mL of 2 M HCl solution at 40 °C. The mixture was stirred for 24 h at the same temperature and then aged at 90 °C for 24 h in closed polyethylene bottles. The recovered white solid was filtered, washed with demineralized water, dried at 110 °C and finally calcined in air at 550 °C for 6 h following a heating rate of 1 °C min^{-1}.

The crystal structure of SBA-15 and Al-SBA-15(x) catalysts was determined by X-ray powder diffraction in a Bruker D8 Advance equipment, with a Cu-Kα X-ray source ($\lambda = 1.5406$ Å) and a Nickel filter at 40 kV and 40 mA. The diffraction patterns were acquired in the range of 2θ from 0.5° to 8° (low angle) and from 5° to 80°. In order to estimate the specific area and pore size distribution of the material by the BET and BJH methods respectively, the samples were outgassed in vacuum for 5 h at 270 °C in a Micromeritics VacPrep 061 Degas System, to eliminate impurities adsorbed on the samples. Then, nitrogen physisorption experiments were performed on a Micromeritics TriStar instrument. The morphology of the materials was analyzed by Scanning Electron Microscopy (SEM) using an Environmental Scanning Electron Microscope JEOL JSM6400 in high vacuum mode, at low voltage (15 kV). High Resolution Transmission Electron Microscopy (HRTEM) images were obtained using a Philips Tecnai TF20 FEG (Field Emission Gun) microscope with an electron acceleration voltage of 200 kV. The solids were ultrasonically dispersed in isopropyl alcohol, and the suspension was collected on carbon-coated grids. The surface acidic properties of the prepared samples were studied by pyridine adsorption followed by FT-IR. All spectra were recorded on a Nicolet 6700 spectrophotometer using pressed discs of pure powder of ~8 mg cm^{-2}, which were activated by outgassing the IR cell at 450 °C during 2 h. The IR experiments were performed using a homemade glass cell with CaF_2 windows, connected to a conventional gas-manipulation-evacuation apparatus. The adsorption experiments consisted of 3 min contact of the activated sample with pyridine vapor (5 Torr), which allows saturation of the available surface. After this, the cell was evacuated at several temperatures and a spectrum was registered after each evacuation.

2.3. Reaction study

Typically, 1.5 g of catalyst and a MeOH/TCp molar ratio of 30:1 were added to 10 g of a mixture of 20 wt% of HPa in TCp, and were charged into a well-mixed stainless steel Parr-5000 batch reactor of 45 mL. The head space was purged with nitrogen for 5 min and pressurized with it at 2 MPa to keep MeOH in the liquid phase. The temperature was then rapidly increased to the corresponding reaction temperature (175 °C, 195 °C or 215 °C), and once the temperature has been reached out, the reactor was maintained in operation under autogenous pressure. Finally, the stirrer speed was increased to 600 rpm, this point was taken as time zero for the reaction. Ending the reaction time (t = 1 h, 2 h, 4 h, 6 h, 8 h and 10 h) the reactor was put into an ice bath to stop the reaction, and then it was depressurized. The catalyst was removed from the reaction mixture by centrifugation and the remaining methanol was eliminated by evaporation at 70 °C. Two phases were formed, the top layer was biodiesel and the bottom one glycerol, which was separated by decantation. Afterward, Na_2SO_4 was added to the products mixture to remove the produced water during the esterification of palmitic acid. The reaction products were analyzed using a Hewlett Packard 5890 gas chromatograph equipped with a HP-2 (30 m × 0.25 mm × 0.25 µm) column and flame ionization detector (300 °C). The identification of reaction products was performed using a TurboMass Perkin Elmer mass spectrometer. To calculate the methyl octanoate (MeOc) yield and TCp conversion, the following equations were used:

$$\%\text{MeOcyield} = (n_{MeOc}/3n_{TCpo}) \times 100 \quad (1)$$

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